AD-A254 873

ATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	June 5, 1992	Technical — 5/31/91 – 6/30/92

4. TITLE AND SUBTITLE
"ERASABLE OPTICAL INFORMATION STORAGE IN THE POLYANILINES"

5. FUNDING NUMBERS
G—N00014-90-J-1559

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8. PERFORMING ORGANIZATION REPORT NUMBER
1992-7

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Sponsoring Agency:
DARPA
3701 N. Fairfax Drive
Arlington, VA 22203-1714

Monitoring Agency:
ONR
800 N. Quincy Street
Arlington, VA 22217-5000

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION / AVAILABILITY STATEMENT
Distribution Unlimited

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

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14. SUBJECT TERMS	15. NUMBER OF PAGES
absorption spectra, photoexcitation, band gap transition, pernigraniline, write erase cycles, time dynamics, signal to noise ratio, poly(o-toluidine)	10
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	UL

OFFICE OF NAVAL RESEARCH

GRANT NO.: N00014-90-J-1559

R & T CODE NO.: A400004DF3

TECHNICAL REPORT NO.: 1992-7

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Accepted for Publication in
Appli. Phys. Lett. (1990)

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June 5, 1992

ERASABLE OPTICAL INFORMATION STORAGE IN THE POLYANILINES

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ABSTRACT

The polyaniline family of polymers exhibits properties that allow for the storage of optical information. Photoexcitation of several forms of polyaniline results in long-lived changes in the absorption spectra, associated with trapped charged defect states. These new absorptions exhibit long lifetimes at low temperatures (below ~250 K), with erasure occurring upon warming the sample. Use in erasable optical information storage devices and in related technologies is discussed.

PACS numbers: 42.80.-f, 71.38.+i, 78.50.-w, 78.65.-s

August 3, 1990

Efforts in recent years to develop erasable optical storage devices have focused on various optical phenomena in a number of materials. The most successful efforts have made use of magneto-optical effects in rare earth–transition metal alloys and amorphous-to-crystalline phase transitions in chalcogenide glasses [1,2]. Numerous other approaches have been proposed, including photochromic effects in organic materials such as TCNQ salts [3] and frequency domain optical storage based on persistent spectral hole burning in a variety of organic and inorganic materials [4,5]. Recently the polyaniline family of conducting polymers has been shown to exhibit a number of interesting optical and photoinduced optical properties [6–8] that indicate that this family of materials holds promise for use as an erasable optical storage medium.

Polyaniline is a large bandgap (E_g ~3.8 eV) polymer that consists of alternating C_6H_4 (phenyl) rings and amine or imine nitrogens, the exact composition depending on the oxidation state. Oxidation of the fully reduced leucoemeraldine base toward the half-oxidized emeraldine base and the fully oxidized pernigraniline base leads to the appearance of an absorption band near 2 eV, which is associated with charge transfer from benzenoid to quinoid groups [9–11]. Photoexcitation of polyaniline via pumping into the 2-eV absorption band or into the 3.8-eV bandgap transition results in the formation of long-lived charged defect states, trapped states, and excitons [8]. Various derivatives of polyaniline, including poly(*o*-toluidine) and poly(2-ethoxyaniline), show similar results [12].

The dominant signature of the long-lived photoinduced defects in polyaniline is an increased absorption that peaks near 1.4–1.5 eV [7,8,12]. The origin of this phenomenon has been proposed [8,13] to result from the sensitivity of the electronic states of polyaniline to rotations of the phenyl rings in and out of the plane formed by the nitrogens in the backbone. The new absorption near 1.4 eV results from the presence of a polaron, described in terms of ring-angle distortions, near a planar quinoid moiety [8,9]. Sufficient π–electron delocalization occurs so as to render this configuration as a bound state [8]. Relaxation to the ground state is hindered because of the positive binding energy of this configuration,

but may also be retarded by interchain packing due to a lack of free volume in the material. Previous experiments have shown that the magnitude of the 1.4-eV photoinduced absorption peak in emeraldine base remains nearly constant for several hours when the sample is held at 80 K [7,8], with shorter lifetimes as the temperature is raised; complete erasure occurs upon heating the sample to room temperature. In addition, the magnitude of this peak varies as the square root of the pump intensity, *i.e.*, $I^{\frac{1}{2}}$.

On the basis of these results we have investigated polyaniline for use as an erasable optical storage medium [14]. Samples of numerous forms of polyaniline and its derivatives have been prepared as thin films or as powders dispersed in KBr pellets. Samples are mounted in a cryostat and cooled in the dark to low temperatures. The fractional change in transmission of each sample, $-\Delta T/T$, near 1.4–1.5 eV is determined using a grating monochromator or a FTIR spectrometer to measure the transmission before and after photoexcitation by an argon-ion laser or a dye laser.

Table I lists several of the sample configurations studied for photoexcitation using the 488-nm or 514-nm lines of an argon-ion laser at power densities of $\sim$400 mW/cm^2. Also included are the lifetimes of $-\Delta T/T$ determined for exponential decay at different temperatures. Magnitudes of $-\Delta T/T$ range from a few percent to greater that 30%, depending on the particular sample studied, the concentration of the sample, and the temperature of the sample. Most notable are those materials with lifetimes of at least several days including pernigraniline base at 77 K, emeraldine poly(*o*-toluidine) at 77 K, and, in particular, pernigraniline poly(*o*-toluidine) at 250 K. The photoinduced absorption of each of these samples showed some initial decay within 1–2 h after photoexcitation, with very little further decay during the measurement time of 18–24 h. Experiments involving longer measurement times are in progress. The results at 250 K for pernigraniline poly(*o*-toluidine) indicate that through molecular design a material *may* be synthesized that possesses long-lived effects at room temperature, which is necessary for practical devices.

As an example of the optical effects observed in these materials, Fig. 1 shows a sample of pernigraniline base in KBr mounted at the end of a liquid nitrogen cold finger. The

sample was exposed to a focused laser beam (488-nm, 100 mW, ~600 μm dia. beam size) whose position was changed to form the pattern "OSU". The photograph was taken using a 35mm camera with infrared film; the illuminating source was the output of a tungsten lamp passed through a long-wavelength-pass filter ($\lambda > 750$ nm) in order to screen out visible light. The increased absorption of the sample is clearly seen as the written pattern "OSU". Changes in intensity of the pattern and the background are due to differences in exposure time of the write beam and due to nonuniformity of the material in the KBr pellet. This written pattern continued to be observed as long as the sample was maintained at low temperature (77 K) and disappeared upon warming the sample to room temperature.

Figure 2 shows a contour plot of the transmission of an emeraldine base film of thickness $\lesssim$0.5 μm on a quartz substrate held at 77 K after being exposed to a pump laser beam at 580 nm of size ~70 μm dia. The transmission was measured using a laser beam at 827 nm (1.5 eV) of size ~30 μm dia. The sample was scanned over a 200 μm square. Small irregularities in the contour reflect variations in sample uniformity in the area probed. Although the maximum photoinduced effect is concentrated within the combined write beam and read beam diameters, the region showing a nonzero photoinduced effect is somewhat larger. This larger size may be due to diffusion of the photoexcited species, slightly unfocussed optics, competition with photoinduced bleaching (because the probe energy is very close to the crossover energy between photoinduced absorption and photoinduced bleaching [8]), and competition with heating effects [15]. Work is currently in progress to determine minimum detectable spot sizes in order to obtain maximum bit storage density.

In addition to studies of lifetimes and bit sizes, other parameters that are important for practical optical information storage have been investigated. Our experiments have shown that there is no degradation with thermal cycling between room temperature and the desired low temperature. Preliminary experiments also indicate that 1.4-eV photoinduced absorption in emeraldine base occurs within a few picoseconds following photoexcitation, so that writing times may be fast. It is estimated that in order to write a 1 μm^2 bit where

$-\Delta T/T \sim 0.1$, an energy of $\lesssim$10 nJ is needed, assuming a square root dependence on write beam energy.

The use of polyaniline or its derivatives for optical information storage would involve the writing of information on a thin film, composite, or blend of polyaniline with a visible or uv laser beam, and subsequently, reading the information with a diode laser (and an appropriate detector) tuned near the peak in the photoinduced absorption spectrum (1.4–1.5 eV). In principle, a sufficiently intense laser operating near 1.4–1.5 eV can be used to heat the exposed portions of the sample to room temperature or higher for erasure of bit information, or the entire sample can be warmed for bulk erasure. The laser-intensity dependence of the photoinduced absorption spectrum may allow for analog data storage at any bit. Other possible uses based on the photoinduced absorption phenomena include photorefractive devices and photoinduced gratings.

In summary, we have found that the polyaniline family of polymers exhibits photoinduced optical absorptions associated with long-lived defect states that make them candidates as media for erasable optical information storage. A variety of forms of polyaniline have been determined to store information for long times with erasure occurring upon heating the sample. Other studies in progress include a survey of additional materials that exhibit similar long-lived optical effects, determination of threshold powers for erasure, maximum bit density, the maximum number of write-erase cycles, time dynamics for writing and erasing, and signal-to-noise ratios for fast reading times. The availability of a broad range of polyanilines, derivatized polyanilines, and similar ring-containing polymers provides a large number of materials options for optical information storage within desired temperature ranges.

This work is supported in part by DARPA through a contract monitored by US ONR. We thank K. A. Coplin and K. Kim for their assistance in these experiments and G. E. Asturias, S. K. Manohar, E. M. Scherr, Y. Sun, and A. G. MacDiarmid for the polymer materials used in this study.

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FIGURE CAPTIONS

Fig. 1: Optical pattern written with the 488-nm argon-ion laser line on a composite pellet of pernigraniline base in KBr mounted at the end of a liquid nitrogen cold finger. The circular hole in the sample holder is 11.5 mm in diameter. The double-ring halo is infrared light reflected from the cryostat.

Fig. 2: Contour plot of the transmission of an emeraldine base film on a quartz substrate held at 77 K. The circular region corresponds to increased absorption in the area where the film was exposed to a $\sim$70-μm size laser beam at $\lambda = 580$ nm and probed with a $\sim$30-μm size laser beam at $\lambda = 827$ nm.

Table I. Materials exhibiting long-lived photoinduced effects.

Material	Temperature (K)	Lifetime
Emeraldine base film	77	110 min
Emeraldine base in KBr	77	24 hr
Pernigraniline base in KBr	77	$\gg$24 hr
Pernigraniline base in KBr	200	>24 hr
Emeraldine poly(*o*-toluidine) in KBr	77	$\gg$24 hr
Emeraldine poly(*o*-toluidine) in KBr	250	$\sim$2.5 hr
Pernigraniline poly(*o*-toluidine) in KBr	77	$\gg$24 hr
Pernigraniline poly(*o*-toluidine) in KBr	250	$\gg$24 hr
Pernigraniline poly(2-ethoxyaniline) in KBr	77	140 min

Fig. 1 R.P. McCall et al.

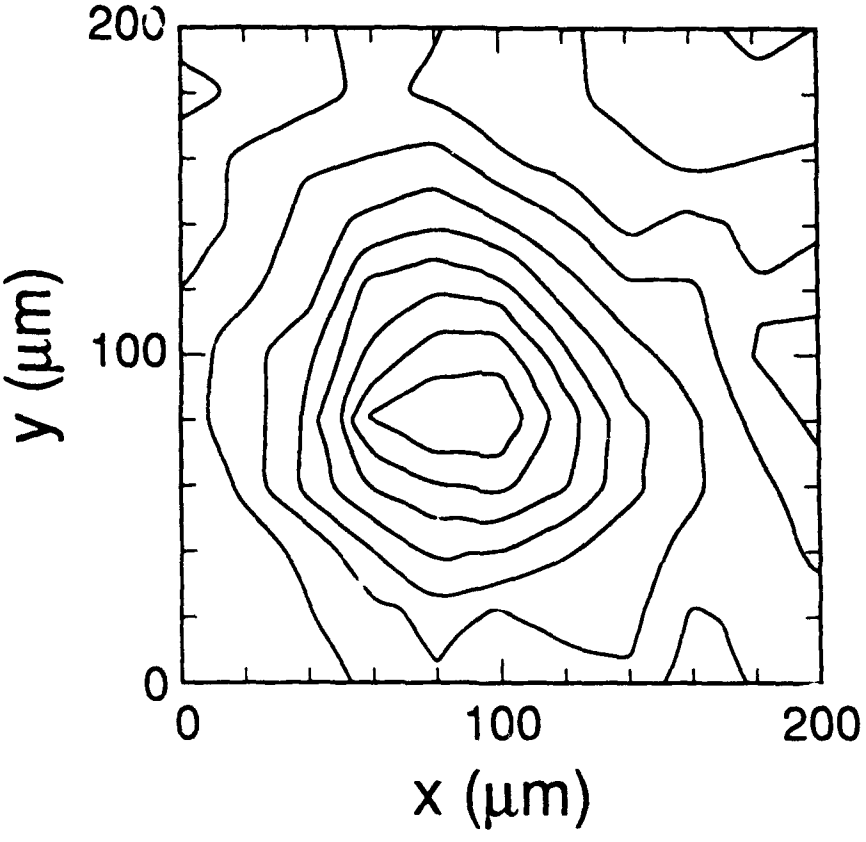

Fig. 2 R.P. McCall et al.

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